PROCEEDINGS

OF

THE ROYAL SOCIETY.

November 16, 1871.

General Sir EDWARD SABINE, K.C.B., President, in the Chair.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair.

Notice was given that at the next Meeting of the Society, H.M. Pedro II., Emperor of Brazil, would be proposed for election and immediate ballot.

Dr. Allman, Dr. Blakiston, Mr. Etheridge, Mr. Newmarch, and Dr. Odling, having been nominated by the President, were elected by ballot Auditors of the Treasurer's Accounts on the part of the Society.

Dr. William Budd, Mr. Carl Schorlemmer, and Mr. Edward Burnet Tylor were admitted into the Society.

The Presents received were laid on the table, and thanks ordered for them.

The following communications were read :—

I. "Considerations on the Abrupt Change at Boiling or Condensing in reference to the Continuity of the Fluid State of Matter." By Professor JAMES THOMSON, LL.D., Queen's College, Belfast. Communicated by Dr. ANDREWS. Received July 4, 1871.

When we find a substance capable of existing in two fluid states different in density and other properties while the temperature and pressure are the same in both, and when we find also that an introduction or abstraction of heat without change of temperature or of pressure will effect the change from the one state to the other, and also find that the change either way is perfectly *reversible,* we speak of the one state as being an ordinary

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gaseous, and the other as being an ordinary liquid state of the same matter; and the ordinary transition from the one to the other we would designate by the terms boiling or condensing, or occasionally by other terms nearly equivalent, such as evaporation, gasification, liquefaction from the gaseous state, &c. Cases of gasification from liquids or of condensation from gases, when any chemical alteration accompanies the abrupt change of density, are not among the subjects proposed to be brought under consideration in the present paper. In such cases I presume there would be no perfect reversibility in the process; and if so, this would of itself be a criterion sufficing to separate them from the proper cases of boiling or condensing at present intended to be considered. If, now, the fluid substance in the rarer of the two states (that is, in what is commonly called the gaseous state) be still further rarefied, by increase of temperature or diminution of pressure, or be changed considerably in other ways by alterations of temperature and pressure jointly, without its receiving any abrupt collapse in volume, it will still, in ordinary language and ordinary mode of thought, be regarded as being in a gaseous state. Remarks of quite a corresponding kind may be made in describing various conditions of the fluid (as to temperature, pressure, and volume), which would in ordinary language be regarded as belonging to the liquid state.

Dr. Andrews (Phil. Trans. 1869, p. 575) has shown that the ordinary gaseous and ordinary liquid states are only widely separated forms of the same condition of matter, and may be made to pass into one another by a course of continuous physical changes presenting nowhere any interruption or breach of continuity. If we denote geometrically all possible points of pressure and temperature jointly, by points spread continuously in a plane surface, each point in the plane being referred to two axes of rectangular coordinates, so that one of its ordinates shall represent the temperature and the other the pressure denoted by that point, and if we mark all the successive boiling- or condensing-points of temperature and pressure as a continuous line on this plane, this line, which may be called *the boiling-line*, will be a separating boundary between the regions of the plane corresponding to the ordinary liquid state and those corresponding to the ordinary gaseous state. But, by consideration of Dr. Andrews's experimental results, we may see that this separating boundary comes to an end at a point of pressure and temperature which, in conformity with his language, may be called the *critical point* of pressure and temperature jointly; and we may see that, from any ordinary liquid state to any ordinary gaseous state, the transition may be effected gradually by an infinite variety of courses passing round outside the extreme end of the boiling-line.

Now it will be my chief object in the present paper to state and support a view which has occurred to me, according to which it appears probable that, although there be a practical breach of continuity in crossing the line of boiling-points from liquid to gas or from gas to liquid, there may exist, in the nature of things, a theoretical continuity across this breach having some real and true significance. This theoretical continuity, from the ordinary liquid state to the ordinary gaseous state, must be supposed to be such as to have its various courses passing through conditions of pressure, temperature, and volume in unstable equilibrium for any fluid matter theoretically conceived as homogeneously distributed while passing through the intermediate conditions. Such courses of transition, passing through unstable conditions, must be regarded as being impossible to be brought about throughout entire masses of fluids dealt with in any physical operations. Whether in an extremely thin lamina of gradual transition from a liquid to its own gas, in which it is to be noticed the substance would not be homogeneously distributed, conditions may exist in a stable state having some kind of correspondence with the unstable conditions here theoretically conceived, will be a question suggested at the close of this paper in connexion with some allied considerations.

It is first to be observed that the ordinary liquid state does not necessarily cease abruptly at the line of boiling-points, as it is well known that liquids may, with due precautions, be heated considerably beyond the boiling temperature for the pressure to which they are exposed. This condition is commonly manifested in the boiling of water in a glass vessel by a lamp placed below, when the temperature of the internal parts of the water, or, in other words, of the parts not exposed to contact with gaseous matter, rises considerably above the boiling-point for the pressure, and the water boils with bumping [*]. At this stage it becomes desirable to refer to Dr. Andrews's diagram of curves showing his principal results for carbonic acid, and to consider carefully some of the remarkable features presented by those curves. In doing so, we have first, in the case of the two curves for 13°·1 and 21°·5, which pass through the boiling interruption of continuity, to guard against being led, by the gradually bending transition from the curve representing obviously the liquid state into the line seen rapidly ascending towards the curve representing obviously the gaseous state, to suppose that this curved transition is in any way indicative of a gradual transition from the liquid towards the gaseous state. Dr. Andrews has clearly pointed out, in describing those experimental curves, that the slight bend at about the commencement of the rapid ascent from the liquid state is to be ascribed to a trace of air unavoidably present in the carbonic acid; and that if the carbonic acid had been absolutely pure, the ascent from the liquid to the gaseous state would doubtless have been quite abrupt, and would have shown itself in his diagram by a vertical straight line, when we regard the coordinate axes for pressures and volumes as being horizontal and vertical respectively. Now in the diagram here submitted the continuous curves (that is to say, those which are not dotted)

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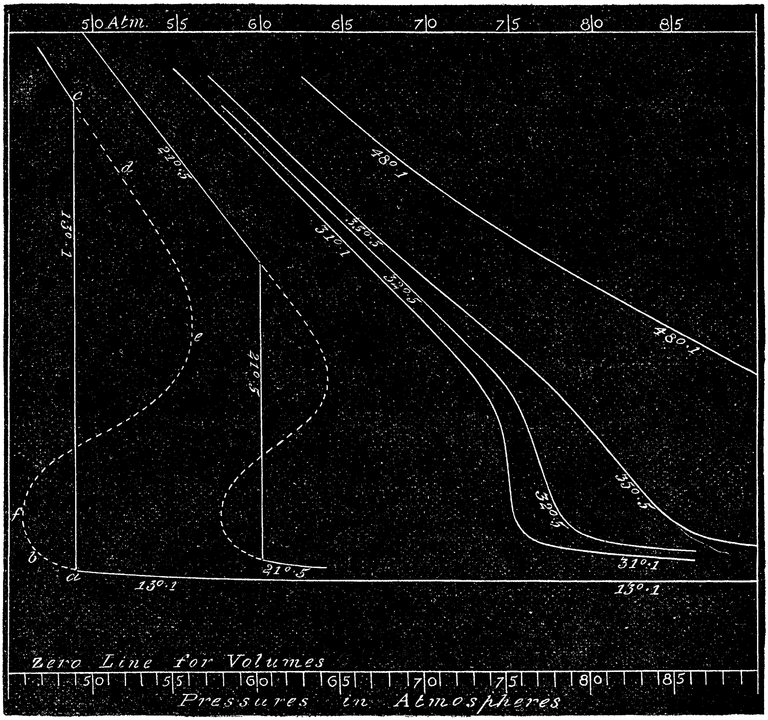
[*] It has even been found by Dufour (Bibliothèque Universelle, Archives, year 1861, vol. xii., "Recherches sur l'ébullition des Liquides) that globules of water floating immersed in oil, so as neither to be in contact with any solid nor with any gaseous body, may, under atmospheric pressure, be raised to various temperatures far above the ordinary boiling-point, and occasionally to so high a temperature as 178° C., without boiling.

On this subject reference may also be made to the important researches of Donny, "Sur la cohésion des Liquides et sur leur adhérence aux Corps solides," Ann. de Chimie, year 1846, 3rd ser. vol. xvi. p. 167.—Jul 28, 1871.



are obtained from Dr. Andrews's diagram, with the slight alteration of substituting, in accordance with the explanations just given, an abrupt meeting instead of the curved transition between the curve for the liquid state and the upright line which shows the boiling stage. Looking to either of the given curves which pass through boiling, and, for instance, selecting the curve for 13°·1, we perceive, from what has been said as to the conditions to which boiling by bumping is due, that for the temperature pertaining to this curve the liquid state does not necessarily end at the boiling pressure for this temperature, and that thus in the diagram the curve showing volumes for the liquid state must not cease at the foot of the upright line which marks the boiling stage of pressure, but must extend continuously, for some distance at least, into lower pressures in some such way as is shown by the dotted continuation from *a* to *b*. But now the question arises, Does this curve necessarily end at any particular point *b*? We know that the extent of this curve in the direction from *a* towards or past *b*, along which the liquid volume will continue to be represented before the explosive or bumping change to gas occurs, is very variable under different circumstances, being much affected by the presence of other fluids, even in small quantities, as impurities in the fluid experimented on, and by the nature of the surface of the containing vessel, &c.

The consideration of the subject may be facilitated, and aid towards the attainment of clear views of the mutual relations of temperature, pressure, and volume in a given mass of a fluid may be gained, by actually making, or by conceiving there to be made, for carbonic acid, from the data supplied in Dr. Andrews's experimental results, a solid model consisting of a curved surface referred to three axes of rectangular coordinates, and formed so that the three coordinates of each point in the curved surface shall represent, for any given mass of carbonic acid, a temperature, a pressure, and a volume which can coexist in that mass. It is to be noticed here that in his diagram of curves the results for each of the several temperatures experimented on are combined in the form of a plane curved line referred to two axes of rectangular coordinates, one of each pair of ordinates representing a pressure, and the other representing the volume corresponding to that pressure at the temperature to which the curve belongs. Now to form a model such as I am here recommending, and have myself made, Dr. Andrews's curved lines are to be placed with their planes parallel to one another, and separated by intervals proportional to the differences of the temperatures to which the curves severally belong, and with the origins of coordinates of the curves situated in a straight line perpendicular to their planes, and with the axes of coordinates of all of them parallel in pairs to one another, and then the curved surface is to be formed so as to pass through those curved lines smoothly or evenly*. The curved surface so obtained exhibits in a very obvious way the remarkable phenomena of the voluminal conditions at and near the critical point of temperature and pressure, in comparison with the voluminal conditions throughout other parts of the range of gradually varying temperatures and pressures to which it extends, and even throughout a far wider range into which it can in imagination be conceived to be extended. It helps to afford a clear view of the nature and meaning of the continuity of the liquid and gaseous states of matter. It does so by its own obvious continuity throughout its expanse round the end of the range of points of pressure and temperature where an abrupt change of volume can occur by boiling or condensing. On the curved surface in the model Dr. Andrews's curves for the temperatures 13°·1, 21°·5, 31°·1, 32°·5, 35°·5, and 48°·1 Centigrade, which afford the data for its construction, may with advantage be all shown drawn in their proper places. The model admits of easily exhibiting in due relation to one another a second set of curves, in which each would be for a constant pressure, and in each of which the coordinates would represent temperatures and corresponding volumes. It may be used in various ways for affording quantitative relations interpolated among those more immediately given by the experiments.

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* For the practical execution of this, it is well to commence with a rectangular block of wood, and then carefully to pare it down, applying, from time to time, the various curves as templets to it, and proceeding according to the general methods followed in a shipbuilder's modelling-room in cutting out small models of ships according to curves laid down on paper as cross sections of the required model at various places in its length.

We may now, aided by the conception of this model, return to the consideration of continuity or discontinuity in the curves in crossing the boiling stage. Let us suppose an indefinite number of curves, each for one constant temperature, to be drawn on the model, the several temperatures differing in succession by very small intervals, and the curves consequently being sections of the curved surface by numerous planes closely spaced parallel to one another and to the plane containing the pair of coordinate axes for pressure and volume. Now we can see that, as we pass from curve to curve in approaching towards the critical point from the higher temperatures, the tangent to the curve at the steepest point or point of inflection is rotating, so that its inclination to the plane of the coordinate axes for pressure and temperature, which we may regard as horizontal, increases till, at the critical point, it becomes a right angle. Then it appears very natural to suppose that, in proceeding onwards past the critical point to curves successively for lower and lower temperatures, the tangent at the point of inflection would continue its rotation, and the angle of its inclination, which before was acute, would now become obtuse. It seems much more natural to make such a supposition as this than to suppose that in passing the critical point from higher into lower temperatures the curved line, or the curved surface to which it belongs, should break itself asunder, and should come to have a part of its conceivable continuous course absolutely deficient. It thus seems natural to suppose that in some sense there is continuity in each of the successive curves by courses such as those drawn in the accompanying diagram as dotted curves uniting continuously the curves for the ordinary gaseous state with those for the ordinary liquid state.

The physical conditions corresponding to the extension of the curve from *a* to some point *b* we have seen are perfectly attainable in practice. Some extension of the gaseous curve into points of temperature and pressure below what I have called the boiling- or condensing-line (as, for instance, some extension such as from *c* to *d* in the figure) I think we need not despair of practically realizing in physical operations. As a likely mode in which to bring steam continuing gaseous to points of pressure and temperature at which it would collapse to liquid water if it had any particle of liquid water present along with it, or if other circumstances were present capable of affording some apparently *requisite conditions for enabling it to make a beginning of the change of state* *, I would suggest the admitting speedily of dry steam nearly at its condensing temperature for its pressure (or, to use a common expression, *nearly saturated*) into a vessel with a piston or plunger, all kept hotter than the steam, and then allowing the steam to expand till by its expansion it would be cooled below its condensing-point for its pressure; and yet I would suppose that if this were done with very careful precautions the steam might not condense, on account of the cooled steam being surrounded entirely with a thin film of superheated steam close to the superheated containing vessel. The fact of its not condensing might perhaps best be ascertained by observations on its volume and pressure. Such an experiment as that sketched out here would not be easily made, and unless it were conducted with very great precautions, there could be no reasonable expectation of success in its attempt; and perhaps it might not be possible so completely to avoid the presence of dust or other dense particles in the steam as to make it prove successful. I mention it, however, as appearing to be founded on correct principles, and as tending to suggest desirable courses for experimenral researches. The overhanging part of the curve from e to f seems to represent a state in which there would be some kind of unstable equilibrium; and so, although the curve there appears to have some important theoretical significance, yet the states represented by its various points would be unattainable throughout any ordinary mass of the fluid. It seems to represent conditions of coexistent temperature, pressure, and volume in which, if all parts of a mass of fluid were placed, it would be in equilibrium, but out of which it would be led to rush, partly into the rarer state of gas, and partly into the denser state of liquid, by the slightest inequality of temperature or of density in any part relatively to other parts. I might proceed to state, in support of these views, several considerations founded on the ordinary statical theory of capillary or superficial phenomena of liquids, which is dependent on the supposition of an attraction acting very intensely for very small distances, and causing intense pressure in liquids over and above the pressure applied by the containing vessel and measurable by any pressure-gauge. That statical theory has fitted remarkably well to many observed phenomena, and has sometimes even led to the forecasting of new results in advance of experiment. Hence, although dynamic or kinetic theories of the constitution and pressure of fluids now seem likely to supersede any statical theory, yet phenomena may still be discussed according to the principles of the statical theory;

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* The principle that "the particles of a substance when existing all in one state only, and in continuous contact with one another, or in contact only under special circum-

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stances with other substances, experience *a difficulty of making a beginning of their change of state*, whether from liquid to solid, or from liquid to gaseous, or probably also from solid to liquid," was proposed by me, and, so far as I am aware, was first announced in a paper by me in the Proceedings of the Royal Society for November 24, 1859 (vol. x. p. 158), and in a paper submitted to the British Association in the same year.

In the present paper, at the place to which this note is annexed, I adduce the like further supposition that *a difficulty of making a beginning of change of state* from gaseous to liquid may also probably exist.

and there may be considerable likelihood that conditions explained or rendered probable under the statical theory would have some corresponding explanation or confirmation under any true theory by which the statical might come to be superseded. With a view to brevity, however, and to the avoidance of putting forward speculations perhaps partly rash, though, I think, not devoid of real significance, I shall not at present enter on details of these considerations, but shall leave them with merely the slight suggestion now offered, and with the suggestion mentioned in an earlier part of the present paper, of the question whether in an extremely thin lamina of gradual transition from a liquid to its own gas, at their visible face of demarcation, conditions may not exist in a stable state having a correspondence with the unstable conditions here theoretically conceived.

II. "Contributions to the History of the Opium Alkaloids.—Part III." By C. R. A. Wright, D.Sc., Lecturer on Chemistry in St. Mary's Hospital Medical School. Communicated by Dr. H. E. Roscoe. Received July 21, 1871.

§ 1. *Action of Hydriodic Acid on Codeia in presence of Phosphorus.*

In Parts I. and II. of these researches the action of hydrobromic acid on codeia and its derivatives has been partially investigated; and as the action of this acid appears to be in some respects similar to, but in others different from, that of hydrochloric acid, it appeared to be of interest to examine the action of hydriodic acid also.

Some preliminary experiments on this subject made two or three years ago in conjunction with the late Dr. A. Matthiessen, showed that when codeia is boiled with a large excess of strong hydriodic acid, no appreciable quantity of methyl iodide is evolved even after some hours' treatment; a brown tarry mass containing much free iodine was produced, but at the time nothing fit for analysis was obtained from this; since then, Dr. Matthiessen and Mr. Burnside* have corroborated the non-formation of methyl iodide under these circumstances.

If, however, phosphorus be added simultaneously with the hydriodic acid, so as to prevent the accumulation of free iodine, methyl iodide is evolved at 100° and upwards in quantity close upon that required for the equation

$$\underset{\text{Codeia.}}{C_{18}H_{21}NO_3}+HI=CH_3I+\underset{\text{Morphia.}}{C_{17}H_{19}NO_3};$$

hitherto, however, no body of this latter formula has been isolated from the products of the reaction, the substances ultimately formed being derived from a base containing H_2 more than morphia.

The hydriodic acid was obtained in the first instance by the action of

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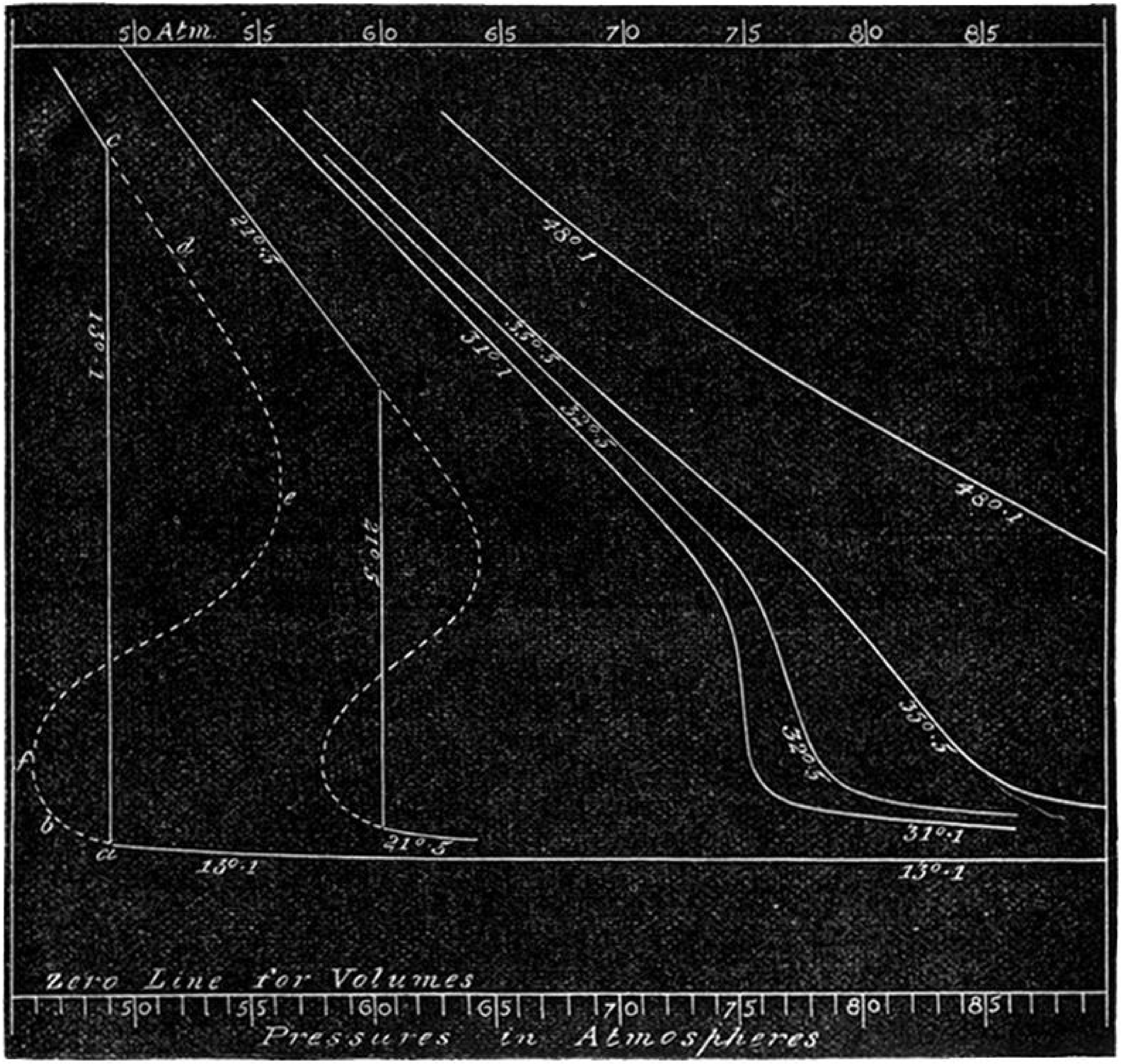
* Proc. Roy. Soc. vol. xix. p. 71.


50 Atm.
55
60
65
70
75
80
85
c
d
e
f
b
a
13°.1
21°.5
31°.1
32°.5
35°.5
48°.1
Zero Line for Volumes
Pressures in Atmospheres